Origin of Dimethoxyserratene derivatives in a peat bog

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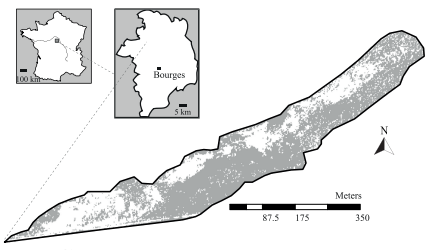
INTRODUCTION

Due to the diversity of their skeleton, functional groups and configurations, pentacyclic triterpenes are molecular biomarkers that are susceptible to provide precious information on past local vegetation. When preserved in natural archives, and considering their taxonomical value, they can be used to track the evolution of past ecosystems through the time. For example, triterpenyl acetates are mainly produced by Asteraceae (Lavrieux et al., 2011) whereas pentacyclic triterpenes methyl ether are essentially biosynthesized by Poaceae (Jacob et al., 2005), both taxa representing open vegetation. Recently, various methoxyserratenes identified in coniferous forest soils (Le Milbeau et al., 2013) have been related to their source organisms, i.e. Pinaceae. Unravelling the past dynamics of this tree group is important because it is implicated in many Human activities (forestry). As part of our continuing effort to identify the source-product relationship between methoxyserratenes and Pinaceae, and to test whether these compounds can be preserved in various archives (soils, peats and sediments), we have analysed peat samples with a focus on these compounds.

MATERIALS AND METHODS:

Peat and plants samples were taken from La Guette peat bog, located in Neuvy-sur-Barangeon (Sologne, Cher) in the French Centre Region (154 m a.s.l.; N 47°19′, E 2°16).

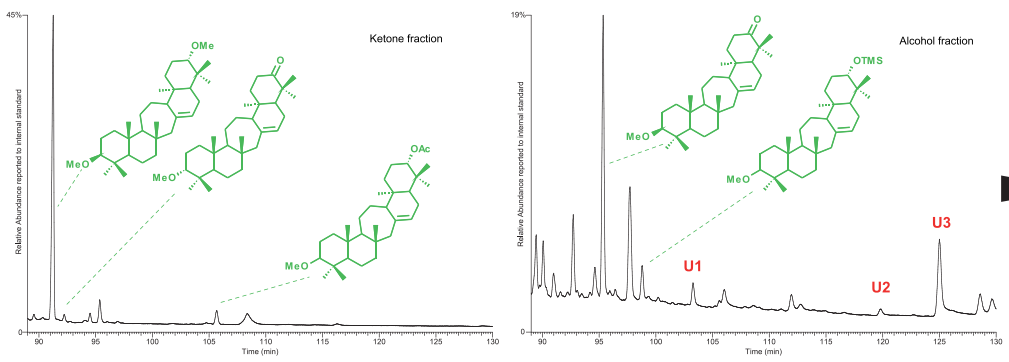
Samples were dried, crushed, and then extracted using Accelerated Solvent Extraction (Dionex ASE 200) with DCM:MeOH (9:1). Lipids were separated into neutral, acidic and polar compounds by flash chromatography on amino-propyl-bonded silica. The neutral fraction was separated into five fractions (aliphatics, aromatics, ethers, ketones and alcohols) on silica gel column with solvent of increasing polarity before be identification by GC-MS.



(Zocatelli et al., 2013)

DISTRIBUTION OF METHOXYSERRATENES IN PEAT SAMPLES

Five compounds were identified as methoxyserratenes.



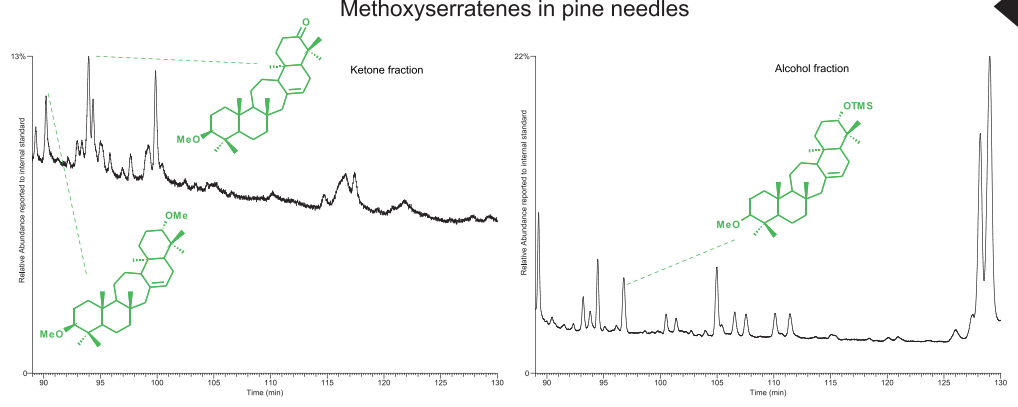
These compounds, known to be biosynthesized by *Pinaceae* (Le Milbeau et al., 2013) originate from *Pinus sylvestris*, which is the only *Pinaceae* growing in this peat bog.

This is the first report of methoxyserratenes in peat samples. This observation attests to the preservation of these biomarkers in this type of soil and to the possibility for these biomarkers to constitute new tools for paleoenvironmental reconstructions.

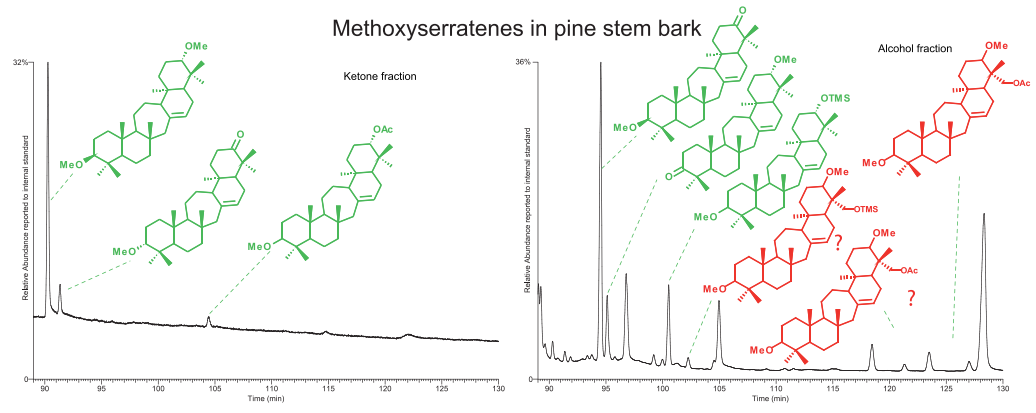
ORIGIN OF NEW OXYGENATED DIMETHOXYSERRATENES

To our knowledge, oxygenated dimethoxyserratenes have never been described. Their possible sources were investigated. *P. sylvestris* present in the surrounding is the more probable the source of methoxyserratenes. We analysed needles and bark of this pine.

Methoxyserratenes in pine needles



Methoxyserratenes in pine stem bark

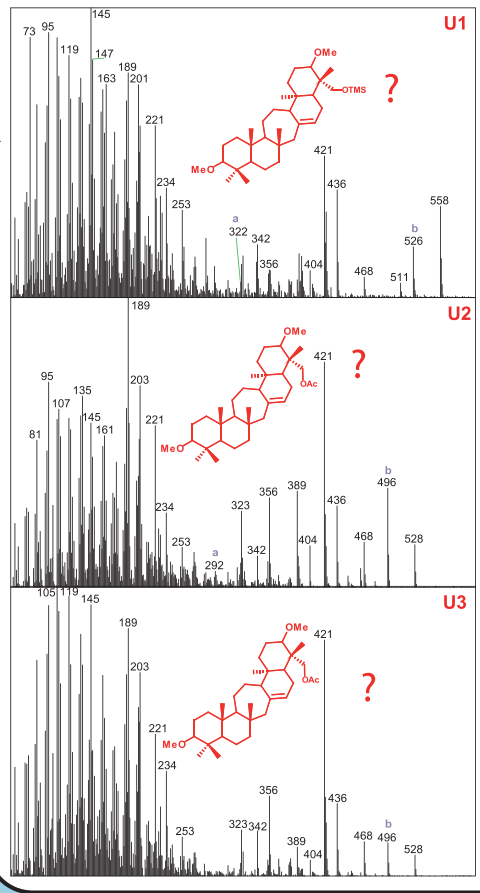


The three new oxygenated dimethoxyserratenes (and the five methoxyserratenes) detected in peat samples are present in *P. sylvestris*, which hence constitute their source.

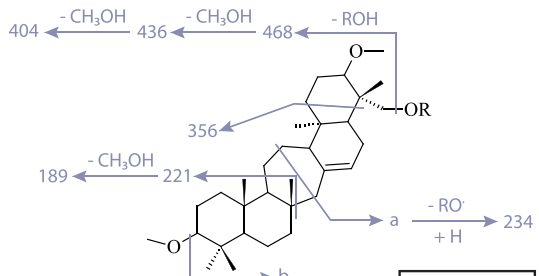
All methoxyserratenes are more abundant in bark than in leaves

IDENTIFICATION OF NEW OXYGENATED DIMETHOXYSERRATENES

Three new serratane-type derivatives (**U1**, **U2**, **U3**) have been detected. These compounds have 2 methoxy groups and an additional oxygenated function



Proposed fragmentation based from Le Milbeau et al. (2013).



	R	
	CH_3CO-	$(CH_3)_3SI$-
a	292	322
b	496	526
	U2, U3	U1

On the basis of their mass spectra, these compounds are identified as :

- **U1** : 29-hydroxy-3,21-dimethoxyserrat-21-ene,
- **U2** : 29-acetoxy-3,21-dimethoxyserrat-21-ene,
- **U3** : 29-acetoxy-3,21-dimethoxyserrat-21-ene.

CONCLUSION

Methoxyserratenes were detected for the first time in peat and confirm the potential these compounds as specific biomarker of *Pinaceae*. Their presence in La Guette peat is explained by their biosynthesis by *Pinus sylvestris* found in the surrounding. Additionally, we report three new natural products found both in *P. sylvestris* and peat samples.

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